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MELT COATING POLYESTER RESIN COMPOSITION

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(54) Title of the invention MELT COATING POLYESTER RESIN COMPOSITION

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SPECIFICATION

1. TITLE OF THE INVENTION

Melt coating polyester resin composition

2. SCOPE OF PATENT CLAIMS

A melt coating polyester resin composition that is characterized in that it is prepared by incorporating one or two or more types of a titanium chelate derived from triethanol amine titanate, dihydroxy-bis(lactic acid) titanate, or dioctyl(phosphate) titanate with a polyester resin composition containing 70% or greater of a polyester resin or polyester imide resin obtained by polycondensation of a multivalent carboxylic acid or a derivative thereof and a polyvalent alcohol.

3. DETAILED DESCRIPTION OF THE INVENTION

The present invention relates to a melt coating polyester resin composition that is suitable as an electrical insulation coating.

Conventional melt coating polyester resin compositions that have been put to many uses as insulation coatings for magnetic

wire and so forth consist of compositions wherein a polyester resin is melted in a phenol solvent such as cresol, xylene, etc.

Recently, to avoid the problems of environmental contamination resulting from these solvents and to improve manufacturability by reducing the number of coats baked on, melt coating methods that reduce the amount of solvent used and that maintain low viscosities by heating the coating vats have been adopted. Looking at this, the polyester compositions generally used in melt coating are compositions wherein a polyester resin obtained by an ester exchange reaction conducted between a polyvalent carboxylic acid whose main constituent is an aromatic dicarboxylic acid, as typified by terephthalic acid, and a polyvalent alcohol and further polycondensed or a polyester imide resin obtained by denaturing a portion of the aforementioned polyester resin with an imide fraction, to which a polymerization catalyst, and as needed, a small amount of solvent is added.

Conventionally, for the polymerization catalyst, a titanium alkoxide, more particularly, tetrabutyl titanate (TBT), tetraisopropyl titanate (TPT), etc., is generally used. However, these have the disadvantage that,

when the polymerization catalyst is added, the viscosity of the solution reaches 1000 poise or greater, so it cannot be combined homogeneously, and when heat is applied for this purpose, the viscosity is reduced and mixing is necessary. As a result, gelling of part or all of the solution occurs and the electrical insulation coating that is the object cannot be obtained. In addition, since the coating is heated and then applied in this method, in coatings combined with a conventional polymerization catalyst, the polymerization reaction proceeds and the increase in viscosity is severe, so that partial or complete gelling occurs and the manufacture of electrical wire, etc., becomes difficult. In order to eliminate these disadvantages, the addition of a compound that is the result of a reaction between, for example, a titanium alkoxide and a low-polymerization polymer or the addition of a titanium chelate followed by a long period of heating at a temperature of 150°C or higher have been studied. However, these have the disadvantage that the time required to synthesize a varnish is too long.

The result of earnest research by the present inventors to solve these problems was the discovery that titanium chelates, such as triethanol amine titanate, dihydroxy-bis(lactic acid) titanate, and dioctyl(phosphate) titanate, are optimal as polymerization catalysts for a melt coating resin composition. That is, these can be heated not only at high temperatures of 150°C or higher, but also at comparatively low temperatures and a homogeneous solution obtained nevertheless, and moreover, these solutions are stable at high temperatures as well and there are no changes at all in viscosity.

With the foregoing background in view, the present invention relates to a melt coating polyester resin composition that is characterized in that it is prepared by incorporating one or two or more types of a titanium chelate derived from triethanol amine titanate, dihydroxy-bis(lactic acid) titanate, or dioctyl(phosphate) titanate with a polyester resin composition containing 70% or greater of a polyester resin or polyester imide resin obtained by polycondensation of a multivalent carboxylic acid or a derivative thereof and a polyvalent alcohol.

The polyester resin used in the present invention is one that is widely used conventionally as an electrical insulation material and is obtained from an ester exchange reaction conducted among a polyvalent carboxylic acid, a polyvalent alcohol, in the presence of a publicly known catalyst such as lead naphthenate or lead acetate as needed, and further polycondensed. The polyvalent carboxylic acid may be terephthalic acid, isophthalic acid, or phthalic acid, etc., or may be an anhydride of these, a low [illegible] alkyl ester such

as dimethyl ester, diethyl ester, or a halide such as a chloride, etc. The polyvalent alcohol may be ethylene glycol, diethylene glycol, trimethylene glycol, tetramethylene glycol, glycerin, diglycerin, trimethylol methane, trimethylol ethane, tris-2-hydroxyethyl isocyanurate (hereafter called THEIC), etc.

Moreover, to produce a polyester imide, it most preferred that an imide carboxylic acid or imide alcohol that includes a five-membered ring imide be used as one or more types of the polyvalent carboxylic acid or polyvalent alcohol. For example, a dicarboxylic acid that includes an imide ring can be obtained by reacting 2 moles of a carboxylic acid anhydride such as trimellitic acid anhydride and 1 mole of a primary diamide. The diamide may be diamino diphenyl methane, diamino diphenyl sulfonate, bisamino propyl(tetraoxaspiro)undecane (hereafter called ATU).

In the present invention, the aforementioned polyester resin is used as is or dissolved in a solvent such as diethylene glycol diethyl ester, diethylene glycol diethylene ester, cresol, xlenol, solvent naphtha, N-methyl-pyrrolidone, etc. The amount of solvent is 30% or less.

The triethanol amine titanate, dihydroxy-bis(lactic acid) titanate, or dioctyl(phosphate) titanate used in the present invention are publicly known as hardening catalysts for water-soluble coatings according to the prior art, but they have not been used as yet as hardening catalysts for the high [illegible] polyester coating according to the present invention.

The suitable amount of titanium chelate additive is 0.01 - 0.05 parts by weight of titanium fraction per 100 parts by weight of resin. With a smaller value than this, hardening of the skin film is extremely slow, and with a larger value than this,

the flexibility and heat deterioration wrapping characteristics are reduced, and thus, such values are not preferred.

This titanium chelate can be heated not only at high temperatures of 150°C or higher, but can be added directly at comparatively low temperatures and the solution is homogeneous at approximately 10 - 30 parts. moreover, In this state, the solution is stable for long periods without gelling.

Next, embodiments of the present invention are explained.

EMBODIMENT 1

Into a 3-liter three-mouth flask were placed 970 g (5 moles) of terephthalic acid dimethyl, 465 g (7.5 moles) of ethylene glycol, and 230 g (2.5 moles) of glycerin and an ester exchange reaction was conducted with 21 g of lead naphthenate as a catalyst. The methanol produced by this reaction was continuously removed from the system. For approximately five hours, the internal temperature was held at 140 - 220°C, and when the methanol was eliminated by distillation, an [illegible] reaction was conducted under a vacuum for a further three hours. Following that, 250 g of diethylene glycol dimethyl ester was added to halt the reaction, and at an internal temperature of 150°C, 30 g of triethanolamine titanate (titanium content: 8%) was added and the mixture was stirred and mixed. Approximately 20 minutes was required to obtain a homogeneous solution. The nonvolatile fraction of this resin solution was 80% (220° for 90 minutes) and the viscosity was 5 poise at 150°C.

COMPARATIVE EXAMPLE 1

When 10 g of tetrabutyl titanate (titanium content: 13.7%) was added in place of the triethanolamine titanate of Embodiment 1 at an internal temperature of 150°C, the entire solution gelled.

COMPARATIVE EXAMPLE 2

The 10 g of tetrabutyl titanate of the Comparative Example 1 was added and mixed over two hours at an internal temperature of 70 - 80°C.

EMBODIMENT 2

Into a 3-liter three-mouth flask were placed 388 g (2 moles) of terephthalic acid dimethyl, 124 g (2 moles) of ethylene glycol, and 92 g (1 mole) of glycerin and an ester exchange reaction was conducted with 8 g of lead naphthenate as a catalyst. The methanol produced by this reaction was continuously removed from the system. For approximately five hours, the internal temperature was held at 140 - 230°C, and when the methanol was eliminated by distillation, 198 g (1 mole) of diamino phenyl methane and 384 g (2 moles) of trimellitic acid anhydride were added at 180°C. Following that, the solution was reacted for four hours at 180 - 220°C, and when the resin became transparent and the reaction distilled water

disappeared, 250 g of cresol was added to halt the reaction, and at an internal temperature of 180°C, 30 g of dihydroxy-bis(lactic acid) titanate (titanium content: 18.4%) was added and the mixture was stirred and mixed to obtain a polyester resin solution. Approximately 10 minutes was required for mixing.

The nonvolatile fraction of this resin solution was 80% (220° for 90 minutes) and the viscosity was 10 poise at 150°C.

COMPARATIVE EXAMPLE 3

The dihydroxy-bis(lactic acid) titanate of Embodiment 2 was replaced with 10 g of tetrabutyl titanate, which was added over approximately one hour at an internal temperature of 70 - 80°C.

The changes in viscosity in the resin compositions according to the aforementioned Embodiments 1 and 2 and Comparative Examples 2 and 3 and the characteristics of insulated wire obtained by melt coating copper wire with a diameter of 1.0 mm with these compositions under the conditions shown in table 1 using a vertical annealing oven with an oven height of 6 meters are shown in Table 1.

Table 1

			Embodiment 1	Embodiment 2	Comparative Example 2	Comparative Example 3
Varnish characteristics	Viscosity change (120°C, poise)	Initial value	30	40	45	50
		After 5 hours	31	42	70	80
Enamel wire manufacture	Coating temperature (°C)		120	120	120	120
	Annealing temperature (°C)		350	350	350	350
	Coatings		2	2	2	2
	Annealing velocity (m/min.)		12	12	12	12
Enamel wire characteristics	Skin film thickness (μ)		22	20	23	20
	Electrical wire external appearance		good	good	cratered	wavy
	Thermal shock resistance		150°C x 1 hr 1 times dia. good	150°C x 1 hr 1 times dia. good	150°C x 1 hr 2 times dia. good	150°C x 1 hr 2 times dia. good
	Softening temperature (°C) (0.8 kg)		320	335	319	330

	Thermal deterioration wrapping	200°C x 6 hr 1 times dia. good	200°C x 6 hr 1 times dia. good	200°C x 6 hr 1 times dia. good	200°C x 6 hr 1 times dia. good
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As is clear from the table, the polyester resin composition according to the present invention showed no change in viscosity at high temperatures and the external appearance of the coating obtained was excellent. In addition, the characteristics compared favorably with those obtained with solvent type coatings according to the prior art, and from the viewpoint of workability, environmental impact, etc., their engineering value was large.

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